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STRUCTURAL SPECIATION ATTEMPTS IN THE BINARY TI(IV)-CITRATE SYSTEM IN AQUEOUS MEDIA

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Abstract

Titanium is an early transition metal, which has found numerous applications. The wide use of titanium in applied materials, ranging from surgical orthopedic prosthetics to various industrial alloys, has prompted pertinent studies targeting the synthesis, spectroscopic, and structural characterization of Ti(IV) species involving the physiologically relevant citric acid. Our initial synthetic efforts on the Ti(IV)-citrate system led to $Na_6[Ti(C_6H_{4.5}O_7)_2(C_6H_5O_7)] \cdot 16H_2O$ *and* $Na_3(NH_4)_3[Ti(C_6H_{4.5}O_7)_2(C_6H_5O_7)\cdot 9H_2O$ *crystalline materials.*

***Key words**: Titanium, citric acid,*

Introduction

Citric acid is an essential biological molecule, well known for its participation in the natural process of oxidation of carbohydrates, fat and proteins, in citric acid cycle (Krebs, 1937). It also appears as a substrate in the active center of aconitase, participating in its transformation to isocitric acid, and finally in mutated forms of the nitrogenase enzyme (Liang, 1990).

Citric acid appears to be an excellent chelator in several interaction systems with metal ions (Burdick, 1983; Widung, 1979), affording efficient formation of complexes. Therefore, it emerges as an essential factor in the environment (Hue, 1986; Matzapetakis, 1998).

Titanium is an early transition metal ion, which has found numerous applications. Titanium regularly constitutes an essential component of alloys used in prosthetic materials destined for orthopedic surgical rectifications in humans, dental fillings, and others.

In all of the aforementioned applications titanium comes in contact with biological tissues, thus giving rise to interactions with a host of biomolecules (Shanbhag, 1997). In the form of Ti(III)-citrate, it has been used extensively in recent years to promote redox reactions involving enzymic functions (i.e. nitrogenase enzyme components) (Jones, 1980). In an effort to peruse binary interactions of Ti(IV) and biologically relevant substrates, we launched research efforts targeting a) the determination of structural speciation of such metal ions in systems interacting with citric acid in aqueous solutions and b) synthesis and subsequent study of the structure and other spectroscopic properties of the requisite compounds.

Experimental

The synthesis of $Na_6[Ti(C_6H_{4.5}O_7)_2(C_6H_5O_7)] \cdot 16H_2O$ and $Na_3(NH_4)_3[Ti(C_6H_{4.5}O_7)_2(C_6H_5O_7)] \cdot 9H_2O$ took place in the open air and in aqueous media (nanopure water), under specific pH (NαOH and NH_3/NαOH were used to provide counter ions to each anionic complex) and temperature conditions. The stoichiometric reactions for the syntheses of complexes of Ti(IV) with citric acid are given in figure 1.

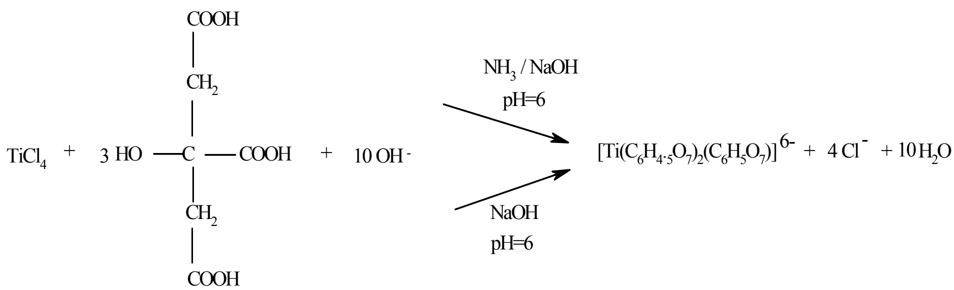

Fig. 1. Reactions for the syntheses of $[Ti(C_6H_{4.5}O_7)_2(C_6H_5O_7)]^{6-}$ complex

Addition of cold ethanol at 4°C resulted after several days in the deposition of a colorless crystalline material. The crystalline products were isolated and characterized spectroscopically and structurally by the following techniques: FT-Infrared (Figure 2) and X-Ray Crystallography (Figure 3).

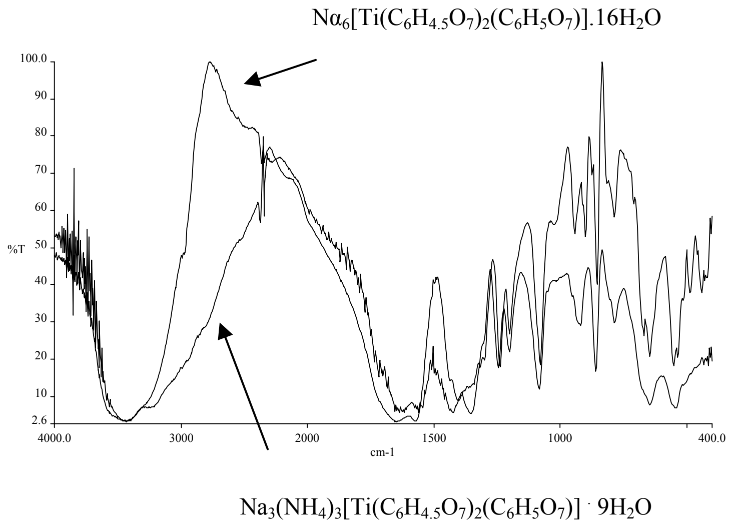

Fig. 2. FT-IR spectra of complexes (**1**) $Na_6[Ti(C_6H_{4.5}O_7)_2(C_6H_5O_7)] \cdot 16H_2O$ and (**2**) $Na_3(NH_4)_3[Ti(C_6H_{4.5}O_7)_2(C_6H_5O_7)] \cdot 9H_2O$

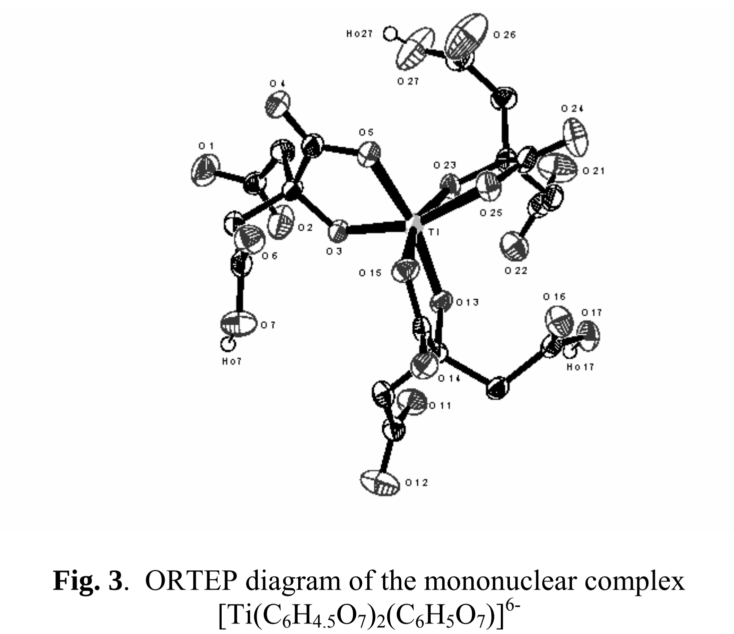

Fig. 3. ORTEP diagram of the mononuclear complex $[Ti(C_6H_{4.5}O_7)_2(C_6H_5O_7)]^{6-}$

Conclusions

In the course of the present investigation, the ability of citric acid to promote complexation chemistry with Ti(IV) was examined. Our studies were carried out in aqueous media and in a wide pH range. Titanium reacted with citric acid in aqueous solution, at pH~6, and afforded the mononuclear anion $[Ti(C_6H_{4.5}O_7)_2(C_6H_5O_7)]^{6-}$, which was isolated in a crystalline form and was characterized structurally and spectroscopically.

Further spectroscopic studies in corroboration with speciation studies on the binary Ti(IV) – citric acid system in aqueous solutions will reveal the potential speciation distributions, which will establish fundamental knowledge on the interactions of that metal ion with biological molecules of variable mass and chemical reactivity.

Such chemical reactivity experiments and biological studies targeting toxicity as well as other biological effects are currently being examined in the lab.

Acknowledgments

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